

Oral Contributions

[MS38] Molecular recognition and complexation in small molecules

Co-Chairs: Alessia Bacchi (IT), Janusz Lipkowski (PL)

[MS38-01] **p-Carboxylatocalix[4]arenes: Controlled Self- and Metal-Directed Assembly.**
Scott J. Dalgarno

Institute of Chemical Sciences, Heriot-Watt University, Riccarton, Edinburgh, EH14 4AS, UK.

E-mail: S.J.Dalgarno@hw.ac.uk

The p-carboxylatocalix[4]arenes represent an underexploited family of building blocks. This is surprising given that the calixarene cavity can be used to form host-guest complexes with suitably sized species, and that the carboxylic acid functionality can be utilized in directed non-covalent assembly with supramolecular synthons (with pyridine derivatives for example). We have recently begun to map out the non-covalent assembly chemistry of these molecules and have developed the ability to engineer structures that possess large solvent-occupied channels of nanometer dimensions.[1] In doing so we have circumvented the propensity to form anti-parallel bi-layers, causing the calixarenes to pack in a parallel fashion, and have also demonstrated the ability to modulate nanotube packing in the solid state.[2-3] In the area of metal-directed assembly we have used the calixarene carboxylic acid functionality to assemble metal-organic assemblies possessing variable distortion that can be readily controlled.[4] This allows for the selective formation of either bi-layer or nanotube structures, with the additional capability of altering the resulting size of the solvent-occupied channels. We have also recently extended these studies to include coordination polymer formation with a range of co-ligands, and in doing so have developed additional methods of accessing metal-organic nanotubes through

ligand cooperativity effects.[5] The position and number of carboxylic acids around the upper-rim of the calixarene framework also has profound effects over metal-directed assembly, driving formation of metal-organic capsules or polymers.[6] These remarkable structural motifs have evolved through the study of the few nanotube systems known, as well as the application of information harvested from the Cambridge Structural Database. Importantly, the results suggest that these molecules are excellent candidates for the controlled formation of many new assemblies that are either discrete or polymeric in nature.

[1] Kennedy, S., Beavers, C.M., Teat, S.J., Dalgarno, S.J. (2011). *New J. Chem.* 35, 28.

[2] Kennedy, S., Dalgarno, S. J. (2009). *Chem. Commun.* 5275.

[3] Kennedy, S., Cholewa, P.P., McIntosh, R.D., Dalgarno, S.J. (2013). *Chem. Commun.* 15, 1520.

[4] Kennedy, S., Karotsis, G., Beavers, C.M., Teat, S.J., Brechin, E.K., Dalgarno, S.J. (2010). *Angew. Chem. Int. Ed.* 49, 4205.

[5] Cholewa, P.P., Beavers, C.M., Teat, S.J., Dalgarno, S.J. (2013). *Cryst. Growth Des.* DOI: 10.1021/cg400125x.

[6] Cholewa, P.P., Beavers, C.M., Teat, S.J., Dalgarno, S.J. (2013). *Chem. Commun.* 48, 3203.

Keywords: calixarenes; self-assembly
supramolecular chemistry; metal-organic
compounds